

Metal Hydrides, MOFs, and Carbon Composites as Space Radiation Shielding Mitigators

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Recently, metal hydrides and MOFs (Metal-Organic Framework/microporous organic polymer composites - for their hydrogen and methane storage capabilities) have been studied with applications in fuel cell technology. We have investigated a dual-use of these materials and carbon composites (CNT-HDPE) to include space radiation shielding mitigation. In this paper we present the results of a detailed study where we have analyzed 64 materials. We used the Band fit spectra for the combined 19-24 October 1989 solar proton events as the input source term radiation environment. These computational analyses were performed with the NASA high energy particle transport/dose code HZETRN. Through this analysis we have identified several of the materials that have excellent radiation shielding properties and the details of this analysis will be discussed further in the paper.

Nomenclature

Al	=	chemical symbol for aluminum
cGy	=	absorbed dose unit: centiGray
CH ₄	=	chemical symbol for methane
CNT	=	carbon nanotubes
ESP	=	Energetic solar particle bow shock enhancement
GLE	=	ground level event (or enhancement)
GOES	=	Geostationary Operational Environmental Satellite
H	=	chemical symbol for hydrogen
HDPE	=	high density polyethylene
HZETRN	=	NASA Langley Research Center-developed high energy particle transport/dose code
Li	=	chemical symbol for lithium
MH	=	metal hydride
MOF	=	metal-organic framework
NASA	=	National Aeronautics and Space Administration
SPE	=	solar proton event

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I. Introduction

RECENTLY, scientists have utilized certain materials “loaded” with hydrogen, namely metal hydrides, to develop fuel cells having various applications, one being the automobile industry¹. Since hydrogen, methane, and other types of hydrocarbons are excellent proton shielding mitigators, we have investigated using hydrogen-loaded metal hydrides along with metal-organic frameworks (MOFs), and nano-porous carbon composites (CNT-HDPE) as potential radiation mitigators. We have found that, indeed, some these materials can serve a dual use for hydrogen storage and proton radiation shielding.

In this paper we present an exhaustive radiation shielding analysis of the results when these selected materials are compared with two baseline materials: aluminum and high density polyethylene (HDPE).

II. Selected Material Groups: Background

The three material groups selected are metal hydrides, MOFs, and carbon composites.

A. Metal Hydrides

Metal hydrides (interstitial, non-interstitial, and solution) most commonly exist within metals or alloys. They are traditionally termed 'compounds', even though they do not strictly conform to the definition of a compound; more closely resembling common alloys such as steel. In such hydrides, hydrogen can exist as either atomic, or diatomic entities. Mechanical or thermal processing, such as bending, striking, or annealing may cause the hydrogen to precipitate out of solution, by degassing. Their bonding is generally considered metallic. Such bulk transition metals form interstitial binary hydrides when exposed to hydrogen. These systems are usually non-stoichiometric, with variable amounts of hydrogen atoms in the lattice. In materials engineering, the phenomenon of hydrogen embrittlement results from the formation of interstitial hydrides. Hydrides of this type forms according to either one of two main mechanisms. The first mechanism involves the adsorption of dihydrogen, succeeded by the cleaving of the H-H bond, the delocalisation of the hydrogen's electrons, and finally, the diffusion of the protons into the metal lattice. The other main mechanism involves the electrolytic reduction of ionised hydrogen on the surface of the metal lattice, also followed by the diffusion of the protons into the lattice. The second mechanism is responsible for the observed temporary volume expansion of certain electrodes used in electrolytic experiments. Interstitial, non-interstitial, and solution metal hydrides were investigated in this study. Those labeled “interstitial” contained new phases after hydrogen loading^{2,7}. The materials labeled “non-interstitial” have expanded lattices after hydrogen loading, but have not been transformed into new structures^{2,4,8}. Finally, those materials labeled “solution” describe materials that do not have transformed crystal structures post-hydrogen loading². There were 40 metal hydrides investigated and they are described in Table 1 and Table 2 below.

Table 1: List of interstitial metal hydrides investigated as part of this study.

Formula	Density (g/cm ³)
91% Li _{2.35} Si and 9% H	0.84
91% LiB and 9% H	0.67
96% CaNi ₅ and 4% H	6.60
96% LaNi _{4.7} Al _{0.3} and 4% H	7.60
96% LaNi _{4.8} Sn _{0.2} and 4% H	8.40
Al ₂ Cu	5.83
Al ₂ CuH	5.39
AlH ₃	2.50
BaAlH ₅	3.30
CaNi ₅	6.60
CaNi ₅ H ₆	5.01
LaNi _{4.7} Al _{0.3}	8.00
LaNi _{4.7} Al _{0.3} H ₆	6.08
LaNi _{4.8} Sn _{0.2}	8.40
LaNi _{4.8} Sn _{0.2} H ₆	6.38
LaNi ₅	8.20
LaNi ₅ H ₆	6.22
Li _{2.35} Si	1.67
LiB	1.65
SrAl ₂ H ₂	2.64
Ti _{0.98} Zr _{0.02} V _{0.48} Fe _{0.09} Cr _{0.05} Mn _{1.5}	7.20
Ti _{0.98} Zr _{0.02} V _{0.48} Fe _{0.09} Cr _{0.05} Mn _{1.5} H _{3.3}	5.80
TiCr _{1.8}	5.70
TiCr _{1.8} H _{3.5}	4.50
TiFe _{0.9} Mn _{0.1}	6.50
TiFe _{0.9} Mn _{0.1} H ₂	5.20

Table 2: List of non-interstitial and solution metal hydrides investigated as part of this study.

Type	Formula	Density (g/cm ³)
Non-Interstitial	LiAlH ₄	0.92
	LiMg(AlH ₄) ₃	1.80
	Mg(AlH ₄) ₂	2.24
	NaAlH ₄	1.81
	VH	5.60
	VH ₂	2.30
	Y ₃ Al ₂ H _{6.5}	4.10
Solution	80% Li and 20% H	0.57
	85% Li and 15% H	0.56
	90% Li and 10% H	0.55
	91% Li and 9% H	0.82
	95% Li and 5% H	0.54
	Li	0.53
	V	6.00

B. Metal-Organic Frameworks (MOFs)

In a recent paper by Ryan J. Kuppler, et al (2009)⁹, the use of hydrogen and methane storage in MOFs is discussed. MOFs are composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. The organic units are typically mono-, di-, tri-, or tetravalent ligands¹⁰. The choice of metal and linker dictates the structure and hence properties of the MOF. For example, the metal's coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation.

There were two types of MOFs investigated for this study, those with hydrogen loading and those without hydrogen loading, for a total of ten materials. The formulas and densities are shown in Table 3 below.

Table 3: The MOFs investigated as part of this study.

	Formula	Density (g/cm ³)
Non-Hydrogen Loaded	Zn ₂₁₆ C ₃₁₃₂ O ₇₀₂ H ₁₂₄₂	0.247
	C ₄₃₂ H ₂₈₈ Be ₄₈ O ₁₄₄	0.423276
	Mg ₁₈ O ₅₄ H ₁₈ C ₇₂	0.905589
	Al ₄ O ₃₂ C ₅₆ H ₄₄	1.610
	C ₂₀₀ H ₁₂₈	0.314945
Hydrogen loaded	Zn ₂₁₆ C ₃₁₃₂ O ₇₀₂ H _{14813.5}	0.2996
	C ₄₃₂ H ₁₁₂₀ Be ₄₈ O ₁₄₄	0.460
	Mg ₁₈ O ₅₄ H ₁₄₁ C ₇₂	0.953
	Al ₄ O ₃₂ C ₅₆ H ₉₆	1.680
	C ₂₀₀ H ₃₂₅	0.3522

C. Nano-porous Carbon Composites (CNT-HDPE)

Dimitra Giasafaki, et al.¹¹ have investigated using nano-porous carbon composites for hydrogen storage:

“Metal-carbon composites have shown considerable hydrogen storage potential at room temperature. In the present work the behaviour of two different Pd amalgam doped carbon substrates, namely a carbogenic foam and a mildly oxidised ordered mesoporous carbon, are compared on the basis of their hydrogen sorption properties at 77 and 298 K and low pressures, aiming to investigate the effect of surface on the storage capacity. In both cases, the introduction of alloy nanoparticles leads to an improvement of the hydrogen uptake with respect to pure carbons. This effect is significant for the carbogenic foam, however small for the ordered carbon.”

For this study, we again looked at two groupings for the CNT-HDPEs. They are those with hydrogen loading and those without hydrogen loading. The formulas and densities for the 14 materials are shown in Table 4.

Table 4: The CNT-HDPEs investigated as part of this study.

	Formula	Density (g/cm ³)
Non-Hydrogen Loaded	(C ₂ H ₄) _{97.7} C _{2.30}	0.95
	(C ₂ H ₄) _{93.27} C _{6.73}	0.96
	(C ₂ H ₄) _{89.06} C _{10.94}	0.97
	(C ₂ H ₄) _{79.41} C _{20.59}	1.00
	(C ₂ H ₄) _{63.16} C _{36.84}	1.04
	(C ₂ H ₄) ₅₀ C ₅₀	1.10
	(C ₂ H ₄) _{39.13} C _{60.87}	1.16
Hydrogen loaded	(C ₂ H ₄) _{97.7} (CH ₃) _{2.3}	0.95018
	(C ₂ H ₄) _{93.27} (CH ₃) _{6.73}	0.96054
	(C ₂ H ₄) _{89.06} (CH ₃) _{10.94}	0.9709
	(C ₂ H ₄) _{79.41} (CH ₃) _{20.59}	1.0018
	(C ₂ H ₄) _{63.16} (CH ₃) _{36.84}	1.0436
	(C ₂ H ₄) ₅₀ (CH ₃) ₅₀	1.1054
	(C ₂ H ₄) _{39.13} (CH ₃) _{60.87}	1.1672

As was described above, most of the materials research for these types of materials has focused on hydrogen storage. In this paper, we have taken these previous studies one step further and investigated a dual-use for these materials as both hydrogen storage and as possible proton radiation mitigators.

III. Radiation Source Term

We used the solar proton integral and differential spectra for the series of solar particle events that occurred during the 19-24 October 1989 time period as shown in Figure 1 based on the Band fitting method^{12,13}. These proton spectra represent three Ground Level Events (GLE) plus one bow shock enhancement (ESP) as indicated in Figure 2.

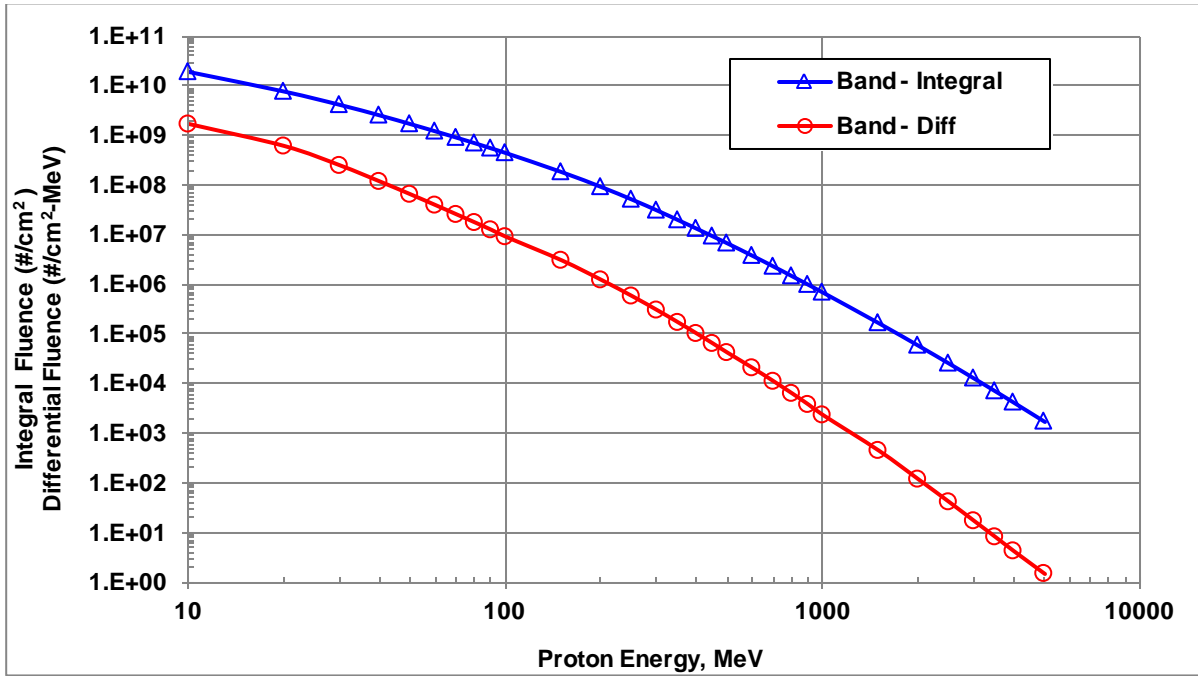


Figure 1: Integral and differential energy spectra for the SPEs occurring 19-24 October 1989.

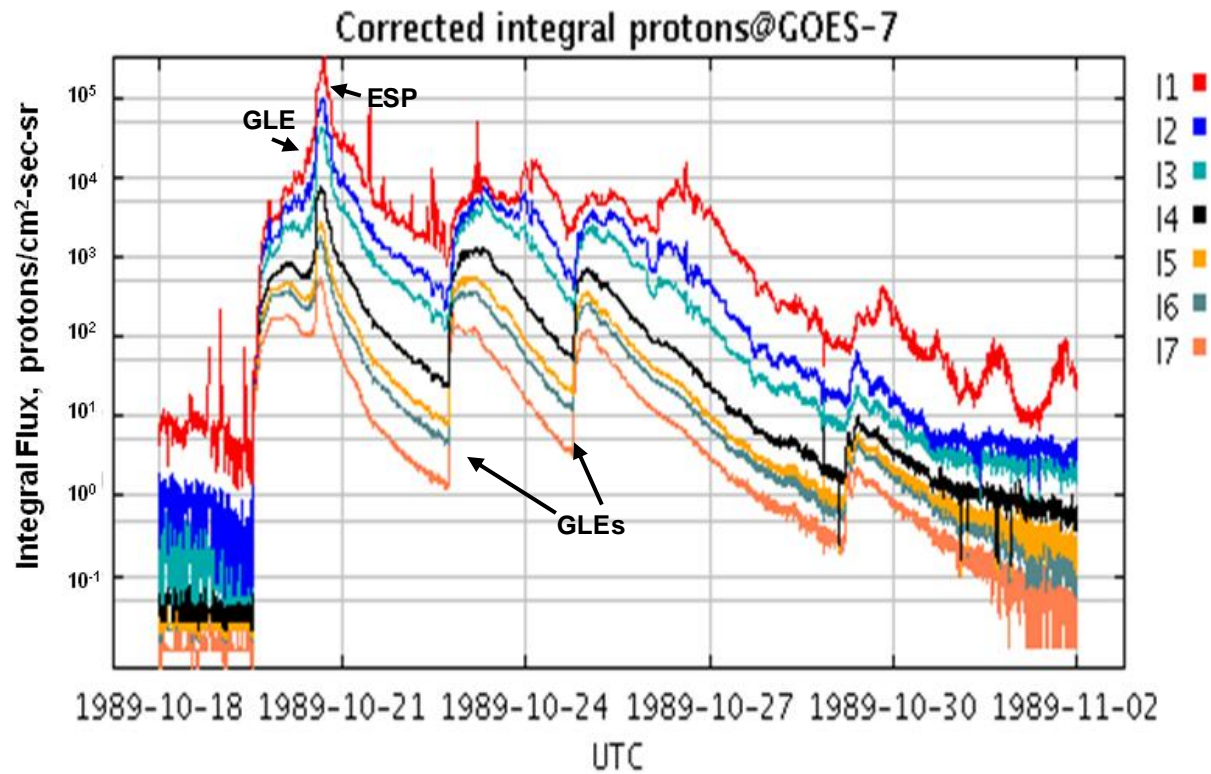


Figure 2: GOES satellite measurements of the four SPEs during the period of 19-24 October 1989. The Ground Level Enhancements (GLE) and Energetic Solar Particle (ESP) are indicated on the plot. The ESP occurs when there is a bow shock enhancement of solar protons. I1: > 1 MeV; I2: > 5 MeV; I3: > 10 MeV; I4: > 30 MeV; I5: > 50 MeV; I6: > 60 MeV; I7: > 100 MeV¹⁴.

IV. Computational Results and Analyses

All the materials in the study were analyzed using HZETRN¹⁵, a one-dimensional formulation of the Boltzmann transport equation with a straight ahead approximation developed at NASA Langley Research Center. The environment chosen for the analysis was the October 1989 series of solar particle events (SPE), which were particularly hard events. The dose in HZETRN includes contributions from neutrons, light ions ($Z=1,2$), and heavy ions. Most of the material doses were computed with the HZETRN 2005 version, since this formulation of the code does not put restrictions on the energy grid for the SPE differential spectrum. In the HZETRN 2005 case, the October 1989 Band fit ranged from 10 to 4992 MeV, and in the HZETRN 2010 version case the energy grid ranged from 0.01 to 2500 MeV, limiting the hard spectrum at the higher energies. The only materials that were investigated with the HZETRN 2010 version of the code were $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{V}_{0.48}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ and $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{V}_{0.48}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{H}_{3.3}$. This is because the HZETRN 2005 version is limited to five species in the material definitions, whereas the HZETRN 2010 version has no limit. Several sample cases were run between the 2005 and 2010 versions of the code and the differences were negligible.

The resulting doses were compared against doses for the two standard radiation shielding materials: aluminum (Al) and high density polyethylene (HDPE). The following (Table 5) gives a summary of the material performances for the 64 materials investigated. As can be seen in the table, there were only nine materials that outperformed HDPE and most of the materials were between the performance of Al and HDPE.

Table 5. Summary of the Material Compared with Al and HDPE

	MOFs	CNTs	MHs	Total
Dose < HDPE	1	7	1	9
HDPE < Dose < Al	9	7	14	30
Al < Dose	0	0	25	25

MOFs

The majority of the MOFs (90%) performed better than aluminum, but not better than HDPE. There was only one material (10%) that was a better mitigator than HDPE (as shown in Figure 3).

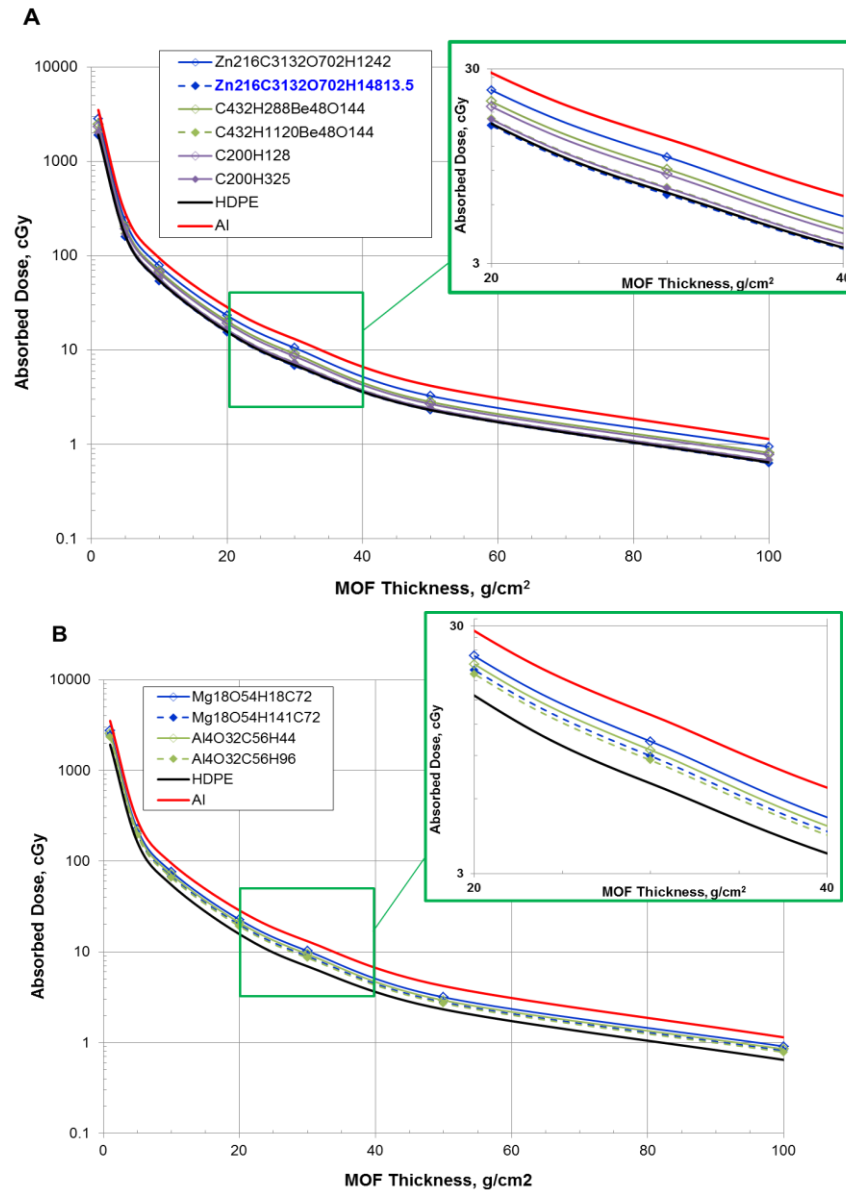


Figure 3: Results from the MOF materials that are compared with Al (red) and HDPE (black). The material that performed better than HDPE is the one highlighted in blue in the legend of the top graph (A).

CNTs

The CNTs were equally split between those materials that were better mitigators than HDPE (50%) and those that performed between that of Al and HDPE (50%). Those that were better than HDPE tended to be the CNTs that were the hydrogenated version of the material (Figure 4).

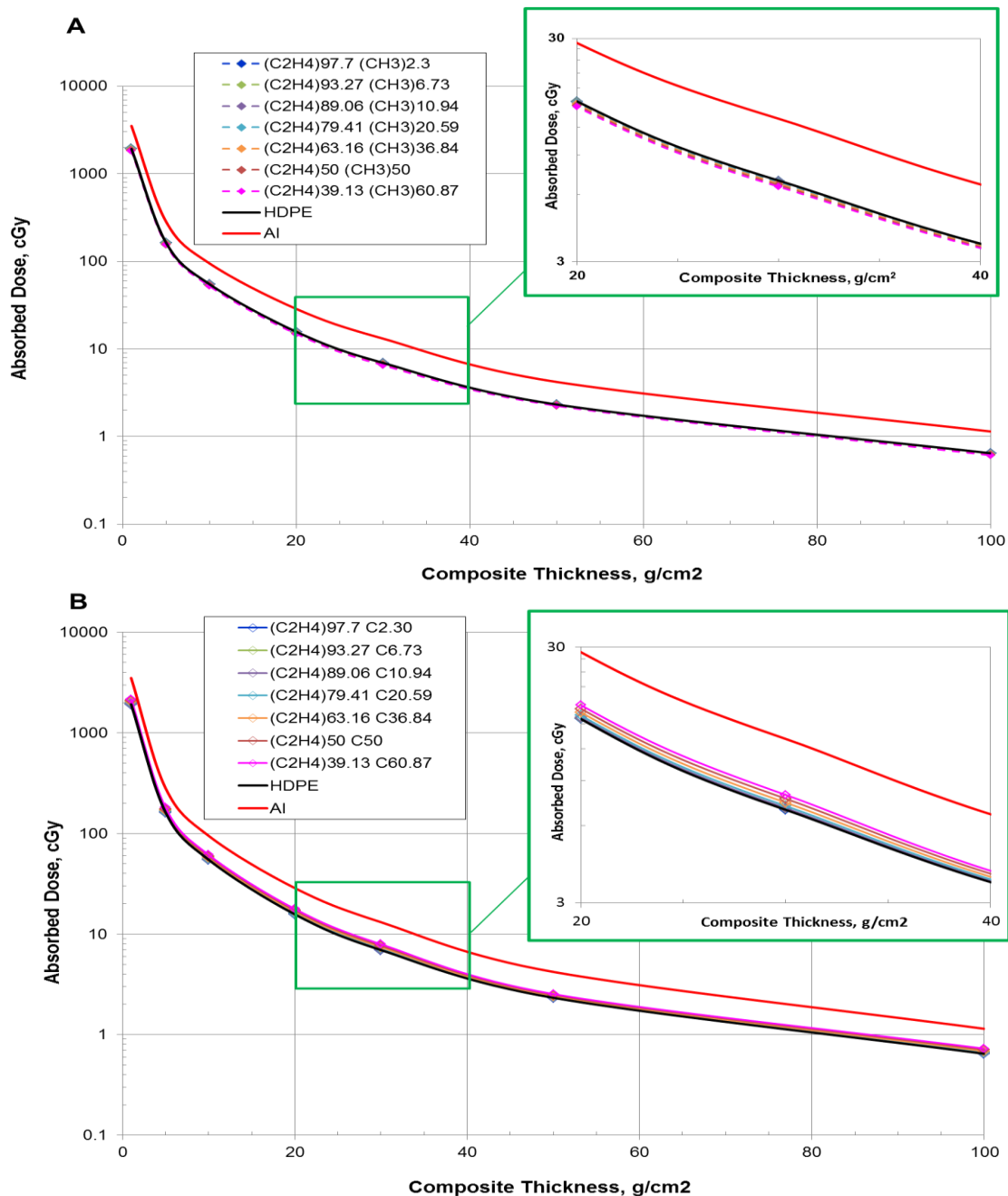


Figure 4: Results from the CNT materials that are compared with Al (red) and HDPE (black). The materials that performed better than HDPE are in the top graph (A) and those that performed better than Al but not HDPE are in the bottom graph (B).

Metal Hydrides

There were several lithium hydrides (Figure 5) investigated, as well as other metal hydrides (Figure 6). Of the metal hydrides, there was only one (2.5%) lithium hydride material that outperformed HDPE (Figure 5). About 35% of the metal hydrides investigated were better mitigators than Aluminum but did not perform better than HDPE (Figure 5 and Figure 6). Approximately 62.5% of the metal hydrides did not perform better than aluminum and are not shown in the figures below.

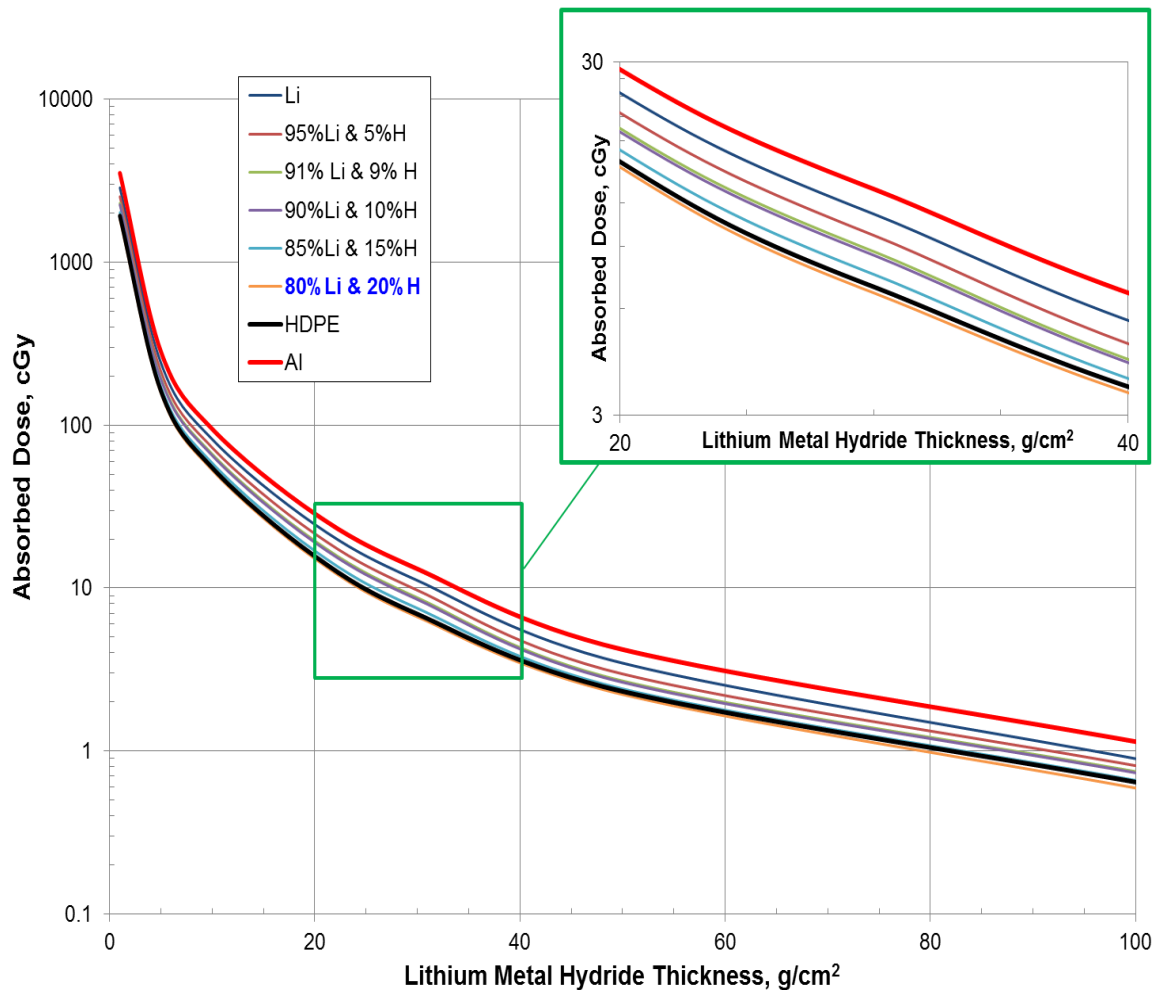


Figure 5: Results from the Lithium and Lithium metal hydride materials that are compared with Al (red) and HDPE (black). The material that performed better than HDPE is the one highlighted in blue in the legend.

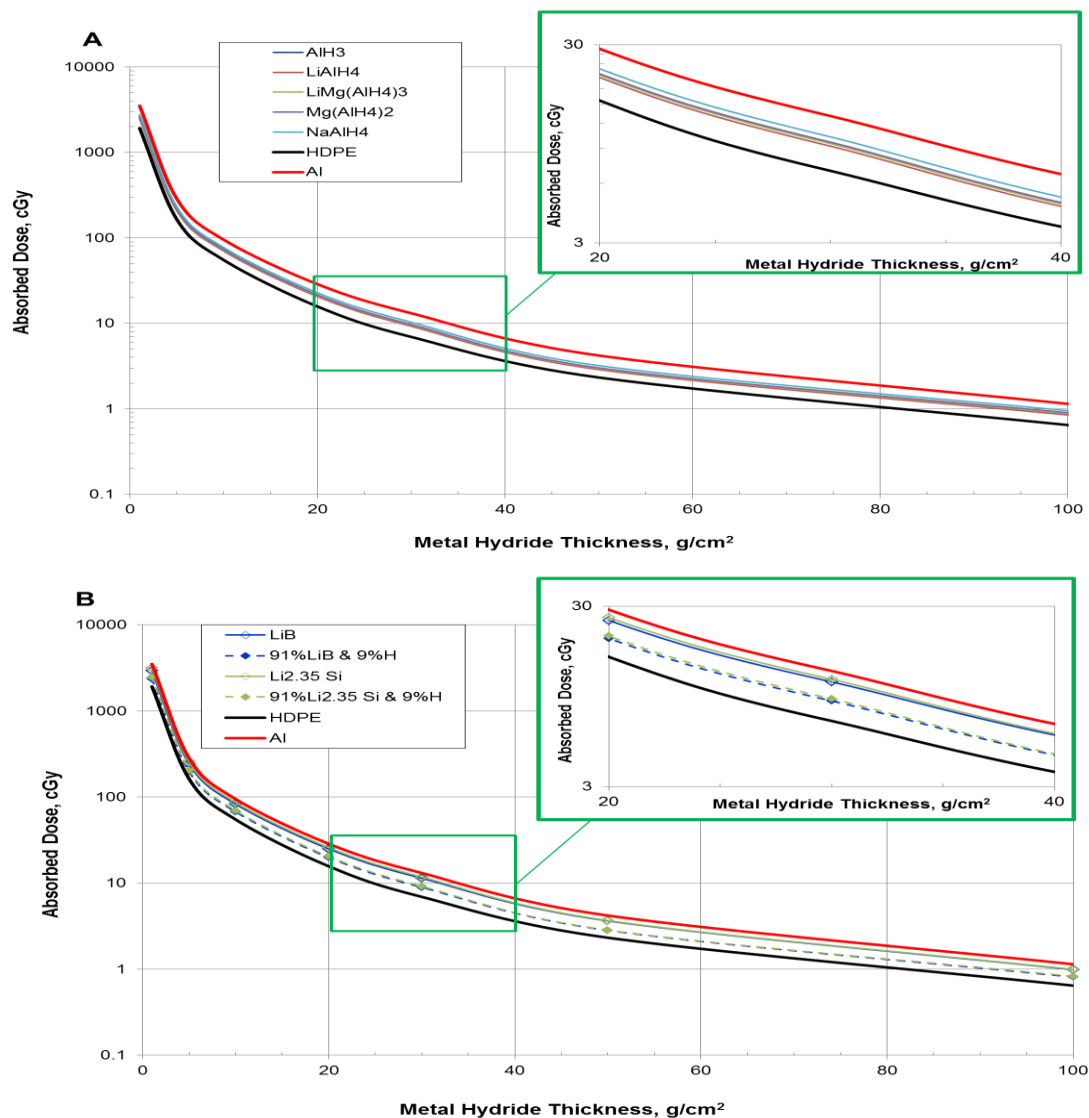


Figure 6: Results from the Metal hydride materials that are compared with Al (red) and HDPE (black). All of these materials performed better than Al.

In addition, we grouped the metal hydrides by three categories: interstitials, non-interstitials, and solution. The results via this grouping are the following.

Number of interstitials: 26

Better than Al, but not as good as HDPE: 19%

Worst than Al: 81%

Number of non-interstitials: 7

Better than Al, but not as good as HDPE: 57%

Worst than Al: 43%

Number of solutions: 7

Better than HDPE: 14%

Better than Al, but not as good as HDPE: 71%

Worst than Al: 14%

V. Summary and Conclusions

In this study, the radiation mitigation potential of 64 materials was investigated and was compared against two standard radiation shielding materials for spaceflight. Of the 64 materials, nine showed improved performance over high density polyethylene, the current “gold standard” of radiation shielding for spaceflight. Of the remaining materials, 30 performed better than aluminum and 25 materials were the worst radiation mitigators of the materials investigated.

Given that 50% of the CNTs outperformed HDPE, future studies should focus on hydrogenated CNTs for radiation shielding development. Another potential grouping of materials for future studies would be the MOFs, which had 10% of the materials showing better mitigation properties than HDPE. It is not recommended to further pursue metal hydrides, since they had the worst performance, with only 2.5% of the materials having better radiation mitigation properties than HDPE. However, if there is further interest in new metal hydrides, those that are non-interstitial or solution types would be of more interest to study than the interstitials.

We also plan to investigate using methane, CH_4 , in place of hydrogen. Figure 7 shows the absorbed dose comparison for HDPE, Al, liquid methane, and liquid hydrogen using the input source term, 19-24 October 1989 differential spectrum. In analyzing the figure below, methane and hydrogen are better mitigators than HDPE, with hydrogen being the best mitigator. While hydrogen repeatedly is the best material for proton shielding in these types of studies, there are problems with using hydrogen in practice. For the purposes of hydrogen-loaded materials, one problem is that hydrogen is not very stable in changing environmental conditions. If the temperature of the environment changes, the hydrogen can leak out of the material. Given that these materials are being considered for spaceflight, large swings in the environmental conditions are typical and the use of a hydrogen-loaded material might not be practical. In addition, hydrogen has large safety implications with respect to fires and explosions. If a hydrogen-doped material were to leach hydrogen as a result of an environmental swing, this could pose some serious safety issues for spacecraft. Thus, given that methane is a comparable radiation shield to hydrogen, our future work will focus on investigating methane-doped versions of these materials to determine whether similar radiation mitigation potential can be found without the concerns posed by hydrogen for space flight.

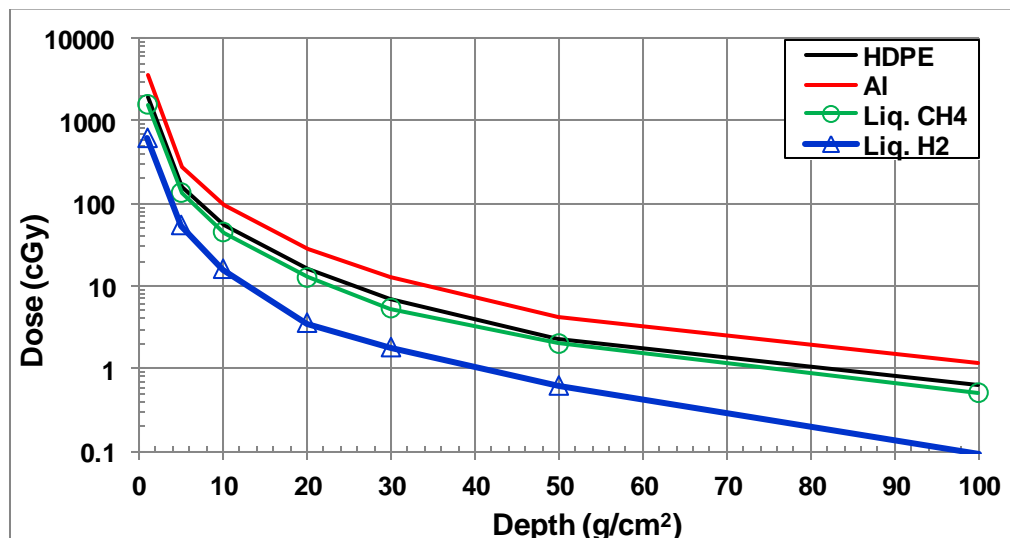


Figure 7: Absorbed dose comparison for aluminum, HDPE, methane, and hydrogen. Input source term: 19-24 Oct 1989 differential spectrum (Band fit).

References

- ¹HiroYuki Saitoh, Shigeyuki Takagi, Naruki Endo, Akihiko Machida, Katsutoshi Aoki, Shin-ichi Orimo, and Yoshinori Katayama. "Synthesis and formation process of Al₂CuH_x: A new class of interstitial aluminum-based alloy hydride," American Institute of Physics (AIP), *APL Materials* **1**, 032113 (2013); doi: 10.1063/1.4821632.
- ²"Final Report on hydrogen storage technology (WP2)", European Commission EESD contract No: ENK-CT=2001-0056, RES-2, 2013.
- ³D. W. Zhou, J. Zhang, P. Peng, J. S. Lu, "Alloying effects on the energy and electronic structures of vanadium hydrides", *Materials Science-Poland*, Vol. 25. No 4, 2007
- ⁴B. Sakintuna, F. Lamari-Darkrim and M. Hirscher, "metal hydrides materials for solid hydrogen storage: a review", *International Journal of Hydrogen Energy*, 32, 1121-1140, 2007
- ⁵S.V. Mitrokhin, "Regularities of hydrogen interaction with multicomponent Ti(Zr)-Mn-V Laves phase alloys", *Journal of Alloys and Compounds* 404-406, p384-387, 2005
- ⁶R. C. Bowman Jr, and B. Fultz, "Metallic hydrides I: hydrogen storage and other gas-phase applications", *MRS Bulletin*, September, 2002.
- ⁷R. Li, S. Zhou, C. Chen, G. Liang, S. Liu and J. Kong, "Quantum chemistry study on electronic structure of vanadium hydrides", *Acta Phys.-Chim*, 21(7), p716-720, 2005.
- ⁸J. Iniguez, T. Yildirim, T. J. Udovic, M. Sulic and C. M. Jensen, "Structure and hydrogen dynamics of pure and Ti-doped sodium alanate", *Physical Review B*, 70, 060191-106101-4, 2004
- ⁹Kuppler, Ryan J., et al., "Potential Applications of Metal-Organic Frameworks," *Coordination Chemistry Reviews* 253 (2009) 3042–3066.
- ¹⁰Czaja, Alexander U.; Trukhan, Natalia; Müller, Ulrich (2009). "Industrial applications of metal-organic frameworks". *Chemical Society Reviews* **38** (5): 1284–1293
- ¹¹Dimitra Giasafaki, et al., "Nanoporous carbon — metal composites for hydrogen storage," *Central European Journal of Chemistry*, October 2011, Volume 9, Issue 5, pp 948-952
- ¹²Tylka, Allan, Dietrich, William, and Atwell, William, "Band Function Representations of Solar Proton Spectra in Ground-Level Events," "38th Scientific Assembly of the Committee on Space Research (COSPAR) Bremen, Germany, 18-25 July 2010.
- ¹³Atwell, William, Tylka, Allan, and Dietrich, William, "Band Function Fit to 23rd Solar Cycle Ground Level Proton Events and Radiation Exposure Assessments," *SAE International Conference on Environmental Systems (ICES)*, Barcelona, Spain, July 9-14, 2010.
- ¹⁴<http://spidr.ngdc.noaa.gov/spidr/>
- ¹⁵John W. Wilson, Francis F. Badavi, Francis A. Cucinotta, Judy L. Shinn, Gautam D. Badhwar, R. Silberberg, C. H. Tsao, Lawrence W. Townsend, and Ram K. Tripathi, "Description of a Free-Space Ion and Nucleon Transport and Shielding Computer Program, NASA Langley Research Center, Hampton, VA, NASA-TP-349, 1995.